



# Removal of 2-nitrophenol by catalytic wet peroxide oxidation using carbon materials with different morphological and chemical properties



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## ABSTRACT

Carbon materials with distinct morphological and chemical characteristics, namely activated carbons, carbon nanotubes, glycerol-based carbon materials and carbon xerogels, were tested for the removal of 2-nitrophenol (2-NP) in aqueous solutions, either by pure adsorption or by catalytic wet peroxide oxidation (CWPO).

The results obtained in adsorption experiments carried out at pH 3,  $T = 323$  K, adsorbent load of  $0.1 \text{ g L}^{-1}$  and 2-NP concentration of  $100 \text{ mg L}^{-1}$ , show that, in general, the activated carbons have superior adsorption performances compared to the other carbon materials tested, exhibiting removals of 2-NP up to  $316 \text{ mg g}^{-1}$  after 150 min of adsorption.

In the CWPO experiments, whilst the activated carbons and carbon xerogels were not able to improve the removal of 2-nitrophenol, in comparison with the removals observed in pure adsorption experiments performed at the same conditions, the use of carbon nanotubes (CNT) and a glycerol-based carbon material (GBCM) resulted in increments in the removal of 2-NP as high as 83% and 56%, respectively. Removals of about 80% after only 30 min and higher than 90% after 150 min of reaction (equivalent to  $929 \text{ mg g}^{-1}$ ) are reached when using CNT as catalysts. The leaching of Fe (present as impurity in the CNT) at the end of the CWPO experiment was found to be negligible. The opposite was observed for classical iron supported on activated carbons, with catalytic activities resulting from the homogeneous contribution of Fe that is leached to the liquid phase. The superior performances found for CNT, makes this catalyst a promising system for CWPO.

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## 1. Introduction

The complexity of industrial wastewaters is increasing nowadays, following the industry's demand towards new products and needs. In particular, nitrophenols are toxic and bio-recalcitrant chemical compounds, inhibitory to some microorganisms [1–5], therefore they can have a negative impact on conventional biological wastewater treatment processes and other treatment options, such as catalytic wet peroxide oxidation (CWPO), should be considered. CWPO, an advanced oxidation process (AOP) involving the use

of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as oxidation source and a suitable catalyst (typically iron based catalysts) to promote its decomposition through the formation of hydroxyl radicals ( $\text{HO}^\bullet$ ), exhibiting high oxidizing potential and serving as effective species in the destruction of a huge range of pollutants [6,7], is especially attractive due to the use of mild conditions, simple equipment and environmental safety of  $\text{H}_2\text{O}_2$  [8]. Although the use of metal catalysts like iron, either directly in solution (*i.e.*, homogeneous catalysis, the so-called Fenton's reaction), or immobilized onto a support (*i.e.*, heterogeneous catalysis, CWPO), might be useful for the degradation and mineralization of organic pollutants in water [9,10], it raises difficulties, like the loss of activity of the heterogeneous catalysts due to Fe leaching [11,12] and/or the need for a complicated final chemical-driven separation step for the removal of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions, which are often generated in quantities greater than the limits allowed by European Union Directives for treated water. Thus, the use of metal-free based catalysts in CWPO is of utmost importance.

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It has been previously shown that carbon materials without any supported phases, mainly activated carbons and activated carbon xerogels, can act as catalysts for the CWPO of organic pollutants in aqueous solutions [13–17].

At the same time, the application of carbon nanomaterials, such as carbon nanotubes, has grown, these materials being nowadays intensively explored in catalysis, either as supports for immobilizing active species or also as catalysts on their own [18,19]. Carbon nanotubes possess high surface areas and their surface chemistry can be easily modified [20]. Likewise, the interest in exploring new forms of carbon materials obtained by *in situ* partial carbonization and sulfonation of natural products, or process by-products, has increased, since they present strong acidic characteristics due the high surface density of sulphonic acid groups [21–23]—which are known to increase the efficiency of the CWPO process [14]. Accordingly, aiming to explore new forms of carbon based materials without any supported phase with potential catalytic activity for CWPO, distinct types of carbon materials were tested in the present work for the removal of 2-nitrophenol (2-NP) from aqueous solutions: commercial activated carbon Norit ROX 0.8 (as received, and chemically modified by liquid phase and thermal treatments); commercial multi-wall carbon nanotubes obtained from Sigma–Aldrich; a glycerol-based carbon material prepared by partial carbonization of glycerol in concentrated sulphuric acid; and a carbon xerogel prepared by polycondensation of resorcinol with formaldehyde. 2-NP was selected as a model compound representative of other non-biodegradable phenols often found in industrial wastewaters, such as those from pharmaceutical, petrochemical, metallurgical, textile, rubber and plastic industries, refineries, fungicides and even from municipal landfill leachate [24–29].

To the best of our knowledge, this work reports for the first time the application of as-produced multi-wall carbon nanotubes, glycerol-based carbon materials prepared by partial carbonization of glycerol and carbon xerogels, without any supported phases, in CWPO of nitrophenolic compounds.

## 2. Materials and methods

### 2.1. Reactants

2-NP ( $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$ , Mr 139.11 [CAS number: 88-75-5], 98 wt.%), iron(III) nitrate nonahydrate (98 wt.%), resorcinol (99 wt.%) and formaldehyde solution (37 wt.% in water, stabilized with 15 wt.% methanol), were purchased from Sigma–Aldrich.  $\text{H}_2\text{O}_2$  (30%, w/v) and sodium hydroxide (98 wt.%) were obtained from Panreac. Sulphuric acid (96–98 wt.%), nitric acid (65 wt.%) and urea (65 wt.%) were obtained from Riedel–de-Haën. Methanol (HPLC grade), glacial acetic acid (analytical reagent grade) and acetonitrile (HPLC grade) were obtained from Fisher chemical. Glycerol (99 wt.%) was obtained from Alfa Aesar. All chemicals were used as received without further purification. Distilled water was used throughout the work.

### 2.2. Carbon materials

Four types of carbon materials were initially considered in this work: the commercial activated carbon Norit ROX 0.8 (AC), a commercial sample of multi-wall carbon nanotubes (>90% carbon basis, O.D.  $\times$  I.D.  $\times$  L: 10–15 nm  $\times$  2–6 nm  $\times$  0.1–10  $\mu\text{m}$ ) obtained from Sigma–Aldrich, ref. 677248 (CNT), a glycerol-based carbon material (GBCM) and a carbon xerogel (CX).

AC is a commercial acid washed extruded activated carbon produced by steam activation, which has a high purity with an ash content of only 3 wt.% (0.02 wt.% Fe). CNT are commercial carbon

nanotubes (Arkema Inc., Graphistrength® C100), grown in iron particles by catalyzed chemical vapour deposition, with contents of alumina and iron oxide under 7 wt.% and 5 wt.%, respectively, and without detectable free amorphous carbon [30–32]. Further characterization of CNT can be found in the literature [33,34].

GBCM was prepared by partial carbonization of glycerol adapting the procedure described elsewhere [22]: a mixture of glycerol (10 g) and concentrated sulphuric acid (40 g) was gently heated to 453 K and left at that temperature for 20 min to allow *in situ* partial carbonization and sulfonation. During heating, the liquid gradually got darker and at 418 K the mixture started to foam intensely and quickly thickened and gained density resulting in a black solid which was then cooled, washed and filtered in warm water until the neutrality of the rinsing waters was reached. The resulting material was then calcined under a nitrogen flow (100 cm<sup>3</sup> min<sup>−1</sup>) at 393 K, 673 K and 873 K during 60 min at each temperature and then at 1073 K for 240 min, defining a heating ramp of 2 K min<sup>−1</sup>.

CX was prepared by polycondensation of resorcinol with formaldehyde (with a molar ratio of 1:2), following the procedure described elsewhere [35]: 9.91 g of resorcinol were added to 18.8 mL of deionised water in a glass flask. After complete dissolution, 13.5 mL of formaldehyde solution were also added. In order to achieve the desired initial pH of the precursor solution (6.1), sodium hydroxide solution was added dropwise under continuous stirring and pH monitoring. The gelation step was allowed to proceed at 358 K during 3 days. After this period the gel was dark red and the consistency of the material allowed the sample to be shaped as desired. The gel was then dried in oven during several days from 333 K to 423 K, defining a heating ramp of 20 K day<sup>−1</sup>. After drying, the gel was pyrolyzed at 1073 K under a nitrogen flow (100 cm<sup>3</sup> min<sup>−1</sup>) in a tubular vertical oven.

Except for the CNT, all the other materials were ground to obtain particle sizes in the range 0.106–0.250 mm.

#### 2.2.1. Modified activated carbons

The powdered original AC was modified by liquid phase, thermal and hydrothermal treatments, resulting in the production of four additional activated carbon samples, following the procedures reported elsewhere [15,36]: a 50 g L<sup>−1</sup> mixture containing AC in concentrated sulphuric acid solution (18 mol L<sup>−1</sup>) was kept for 3 h at 423 K in a 500 mL round-bottom flask heated by an oil bath; the recovered solids were thoroughly washed with distilled water until the neutrality of the rinsing waters was reached, and further dried in an oven for 18 h at 383 K, resulting in the ACS materials. A 50 g L<sup>−1</sup> mixture containing AC in nitric acid (5 mol L<sup>−1</sup>) was kept for 3 h at boiling temperature, and further dried in an oven for 18 h at 383 K, resulting in the ACN materials; a 40 g L<sup>−1</sup> mixture containing ACN in urea solution (1 mol L<sup>−1</sup>) was kept in a 125 mL stainless steel high pressure batch reactor under its own atmosphere at 473 K for 2 h, the recovered solids being thoroughly washed with distilled water until the neutrality of the rinsing waters, and further dried overnight in oven at 383 K, resulting in the ACNU materials; a gas phase thermal treatment was then applied, in which 1 g of ACNU was heated, under a nitrogen flow (100 cm<sup>3</sup> min<sup>−1</sup>), at 393 K, 673 K and 873 K during 60 min at each temperature and then at 1073 K for 240 min, resulting in the ACNUT materials.

#### 2.2.2. Iron supported activated carbons

Classical iron catalysts supported on activated carbons were prepared using AC and ACS as supports, adapting the procedure described elsewhere [12]: a carbon sample was impregnated by incipient wetness with an aqueous solution of iron nitrate nonahydrate in order to obtain 4 wt.% Fe in the catalyst, dried at room temperature for 24 h, followed by overnight drying at 383 K and calcination in air atmosphere for 4 h at two different temperatures,

473 K and 573 K. The resulting materials were identified as Fe<sub>473</sub>/AC, Fe<sub>573</sub>/AC, Fe<sub>473</sub>/ACS and Fe<sub>573</sub>/ACS, where 473 and 573 represents the calcination temperature.

### 2.3. Characterization techniques

The textural properties of all tested materials were calculated from N<sub>2</sub> adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVA 4200e adsorption analyser. The specific surface area ( $S_{\text{BET}}$ ) was obtained by applying the BET method to the collected isotherms and the non-microporous surface area ( $S_{\text{Non-mic}}$ ) and the micropore volume ( $V_{\text{Mic}}$ ) were obtained by the t-method. The total pore volume ( $V_{\text{Total}}$ ) was calculated at  $P/P_0 = 0.995$ .

The point of zero charge (PZC) was determined by the pH drift method following the procedure described elsewhere [37]: five solutions with varying initial pH were prepared using HCl and NaOH solutions (0.02 mol L<sup>-1</sup> and 1.0 mol L<sup>-1</sup>) and NaCl (0.01 mol L<sup>-1</sup>) as electrolyte. 50 mL of each solution was contacted with 0.15 g of carbon sample and the suspension stirred for 24 h before the equilibrium pH was measured. The PZC value of each carbon sample was determined by intercepting the obtained final pH vs. initial pH curve with the straight line final pH = initial pH [38,39].

The concentration of acidic active sites on the materials surface was determined by adding 0.2 g of each sample to 25 mL of a 0.02 mol L<sup>-1</sup> NaOH solution. The resulting suspensions were left under stirring for 48 h at room temperature. After filtration, to remove the solid material, the unreacted OH<sup>-</sup> was titrated with a 0.02 mol L<sup>-1</sup> HCl solution. The initial concentration of acidic functionalities was then calculated by the difference between the amount of NaOH initially present in the suspension and the amount of NaOH determined by titration and dividing this value by the mass of material. The concentration of basic active sites was determined in a similar way: this time by adding the carbon sample to a 0.02 mol L<sup>-1</sup> HCl solution and titration with a 0.02 M NaOH solution. Phenolphthalein was used as indicator in both titrations.

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409 PC to determine the carbon content of the CNT after the CWPO run. For that purpose, the sample was heated in air atmosphere from 323 K to 1273 K at 10 K min<sup>-1</sup>. X-ray diffraction (XRD) analysis was performed in a PANalytical X'Pert MPD equipped with a X'Celerator detector and secondary monochromator (Cu K $\alpha$   $\lambda = 0.154$  nm; data recorded at a 0.017° step size).

### 2.4. 2-Nitrophenol removal experiments

Batch pure adsorption and CWPO experiments were performed in a 500 mL well-stirred (500 rpm) glass reactor, equipped with a condenser, a temperature measurement thermocouple, a pH measurement electrode and a sample collection port. The reactor was loaded with 250 mL of a 2-NP aqueous solution (100 mg L<sup>-1</sup>) and heated by immersion in a water bath at controlled temperature. Upon stabilization at the desired temperature, the solution pH was adjusted to 3 by means of H<sub>2</sub>SO<sub>4</sub> and NaOH solutions (1.0 mol L<sup>-1</sup> and 0.02 mol L<sup>-1</sup>) and the experiments were allowed to proceed freely, without further conditioning of the pH. Nevertheless, the evolution of pH along the experiments was monitored and no significant change of the initial pH value was observed. Typical experiments were conducted during 150 min, at  $T = 323$  K, pH 3 and adsorbent/catalyst load = 0.1 g L<sup>-1</sup>.

Pure adsorption runs were performed in order to discriminate between the adsorption and catalytic components of the 2-NP removal by CWPO, but, in this case, the precise amount of adsorbent was added after pH adjustment, in order to reach the desired adsorbent load in solution and defining this instant as  $t_0 = 0$  min.

Following the conditions used in the works recently developed by our group [14,15,17], a calculated volume of H<sub>2</sub>O<sub>2</sub> (6 wt.%) was injected into the system after catalyst addition, in order to reach a concentration ( $C_{\text{H}_2\text{O}_2}$ ) of 34.6 mmol L<sup>-1</sup> in the CWPO runs (three times the stoichiometric amount needed to completely mineralize 2-nitrophenol), being that moment considered as  $t_0 = 0$  min. Blank experiments, without any catalyst, were carried out to assess possible non-catalytic oxidation promoted by H<sub>2</sub>O<sub>2</sub>. Furthermore, iron nitrate nonahydrate was used as Fe<sup>3+</sup> source in homogeneous CWPO runs.

Selected experiments were performed in triplicate, in order to assess reproducibility and error of the experimental results. It was found that the confidence interval was never superior to 2%, considering 99% certainty.

### 2.5. Analytical methods

Both in pure adsorption and in CWPO runs, 1.5 mL samples were periodically withdrawn from the reactor to determine 2-NP concentration by high performance liquid chromatography (HPLC), adapting the procedure previously described [40]. For that purpose, a Jasco HPLC system equipped with an UV/Vis detector (UV-2075 Plus), a quaternary gradient pump (PU-2089 Plus) for solvent delivery (1 mL min<sup>-1</sup>) and a Kromasil 100-5-C18 column (15 cm  $\times$  4.6 mm; 5  $\mu$ m particle size) was used. Mobile phase consisted in an isocratic method of A:B (40:60) mixture of 3% acetic acid and 1% acetonitrile in methanol (A) and 3% acetic acid in ultrapure water (B). The maximum absorbance for 2-NP was found at 277 nm, determined by the analysis of the respective spectrum obtained by UV-vis spectrophotometry (Jasco V530).

For Fe leaching measurements, the remaining solution at the end of CWPO experiments was filtered and the Fe content determined by atomic absorption, using an atomic absorption spectrometer (Varian Spectra 220). The total organic carbon (TOC) was also determined at the end of the CWPO run carried out with CNT, using a Shimadzu TOC-5000A analyser, and the formation and evolution of carboxylic acids was monitored by HPLC, adapting a procedure described elsewhere [36]. For that purpose a Hitachi Elite LaChrom HPLC system equipped with an UV detector (UV L-2400), a quaternary gradient pump (L-2130) for solvent delivery (0.6 mL min<sup>-1</sup>) and a Bio-Rad Aminex HPX-87H column (300 mm  $\times$  7.8 mm; 9  $\mu$ m particle size), was used. A sulphuric acid solution (4 mmol L<sup>-1</sup>) was used as mobile phase. The UV detector was set to 210 nm.

In the samples collected from CWPO runs, an excess of sodium sulphite was immediately added to consume residual H<sub>2</sub>O<sub>2</sub> and instantaneously stop the reaction [41,42].

## 3. Results and discussion

### 3.1. Textural and surface chemistry characterization

The textural properties of the tested carbon materials, determined as described in Section 2.3, are summarized in Table 1. As observed, AC is essentially a microporous material ( $V_{\text{Mic}}/V_{\text{Total}}$  higher than 0.5), characterized by a high surface area and possessing the highest value of  $S_{\text{BET}}$  amongst the initial four carbon materials. In the opposite side, GBCM is a non-porous material, with a  $V_{\text{Total}}$  of 0.02 cm<sup>3</sup> g<sup>-1</sup>. As a consequence, GBCM presents the lowest specific surface area amongst the initial four carbon materials. CNT are essentially non-microporous materials, with  $V_{\text{Mic}} = 0$  cm<sup>3</sup> g<sup>-1</sup>. Even though CNT present a significant specific surface area and a  $V_{\text{Total}}$  above 1 cm<sup>3</sup> g<sup>-1</sup>, which is primarily due to adsorption on the external surface of the tubes [43] and to adsorption on the surface of the inner cavities of some opened CNT (the measured specific surface area is slightly superior to the calculated

**Table 1**

Specific surface area ( $S_{\text{BET}}$ ,  $\pm 10 \text{ m}^2 \text{ g}^{-1}$ ), non-microporous surface area ( $S_{\text{Non-mic}}$ ,  $\pm 10 \text{ m}^2 \text{ g}^{-1}$ ), micropore volume ( $V_{\text{Mic}}$ ,  $\pm 0.01 \text{ cm}^3 \text{ g}^{-1}$ ) and total pore volume ( $V_{\text{Total}}$ ,  $\pm 0.01 \text{ cm}^3 \text{ g}^{-1}$ ) of the carbonaceous materials.

Material	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$S_{\text{Non-mic}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_{\text{Total}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{Mic}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{\text{Mic}}/V_{\text{Total}}$
AC	850	190	0.61	0.33	0.54
CNT	248	279	1.01	0.00	0.00
GBCM	10	10	0.02	0.00	0.00
CX	650	240	1.09	0.19	0.17
ACS	850	190	0.60	0.33	0.55
ACN	873	196	0.61	0.31	0.52
ACNU	902	218	0.61	0.31	0.52
ACNUT	1055	239	0.63	0.34	0.55
Fe <sub>473</sub> /AC	857	152	0.59	0.33	0.56
Fe <sub>573</sub> /AC	1117	193	0.77	0.44	0.57
Fe <sub>473</sub> /ACS	904	189	0.68	0.32	0.48
Fe <sub>573</sub> /ACS	1140	226	0.79	0.40	0.51

geometric area, suggesting that a few CNT have some open ends). CX is a typical mesoporous material, with a ratio  $V_{\text{Mic}}/V_{\text{Total}}$  of 0.17.

Analysing the results given in Table 1 concerned to the activated carbon samples produced by modification of the original AC, it is observed that all treatments led to the development of porosity, although not to an appreciable extent. In the case of the material resulting from the treatment with concentrated sulphuric acid (ACS), the increment in porosity is due to the development of micropores, since it presents the same value of  $S_{\text{Non-mic}}$  but a slightly higher ratio  $V_{\text{Mic}}/V_{\text{Total}}$  when compared to the original AC. The successive chemical treatments with concentrated nitric acid (ACN) and urea (ACNU), as well as the thermal treatment (ACNUT), mainly led to a slight development of mesopores, since the  $S_{\text{Non-mic}}$  value successively increases as the materials are subjected to new treatments, without any notorious modification in microporosity. Finally, according to the calcination temperature applied when preparing the iron supported activated carbon samples, the incorporation of iron on AC and ACS led to two distinct situations: first, when calcination at 473 K is considered, the resulting materials (Fe<sub>473</sub>/AC and Fe<sub>473</sub>/ACS) do not reveal substantial changes in relation to the textural properties of the supports (AC and ACS, respectively); on the other hand, the incorporation of iron with further calcination at 573 K led to the development of porosity, both micro and mesopores.

The general surface chemical properties of the carbon materials were also determined, the corresponding values being gathered in Table 2. It can be seen that AC and CX possess an evident basic character, with a concentration of basic functionalities higher than the concentration of acidic functionalities and a *PZC* above 7. CNT also have a basic character, with a *PZC* of 8.1, but in this case possessing a concentration of acidic functionalities greater than the

concentration of basic functionalities, suggesting the presence of strong basic groups and weak acidic groups. In contrast, GBCM, due to the presence of high amounts of sulphonic acid groups, is characterized as a strong solid acid carbon material [22], as revealed by its low *PZC* value of 1.3. As expected, the materials resulting from the chemical treatments of AC with concentrated sulphuric acid and with nitric acid exhibit a pronounced acidic character, with *PZC* values in the range 1.6 to 2.0. The introduction of N functionalities, upon chemical treatment with urea, increases the *PZC* of the resulting material (ACNU) up to values near neutrality, followed by a substantial decrease of acidic active sites and a large increase of basic active sites; the subsequent thermal treatment enables the production of a material with basic character (ACNUT). All the materials resulting from Fe incorporation on AC and on ACS possess a markedly acidic character, with a high concentration of acidic functionalities.

### 3.2. Adsorption experiments

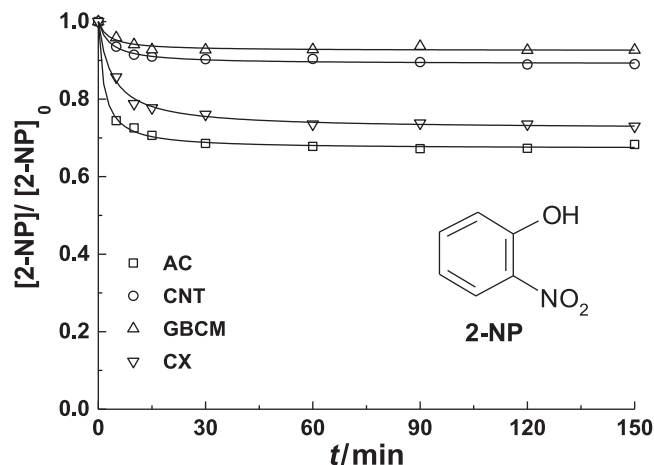
Pure adsorption experiments were carried out to evaluate the ability of the initial four carbon materials to adsorb 2-NP and thus, to discriminate between the adsorption and catalytic components of the 2-NP removal by CWPO. The corresponding removal curves, obtained under the typical conditions referred in Section 2.4, are collected in Fig. 1. The main observation evidenced is that AC is able to adsorb 2-NP with a superior performance than the other materials, followed by CX. Since the origins of the carbon materials considered in this work are completely different, the establishment

**Table 2**

Acid–base properties ( $\pm 10 \mu\text{mol g}^{-1}$ ) and point of zero charge (*PZC*,  $\pm 0.1$ ) of the carbonaceous materials.

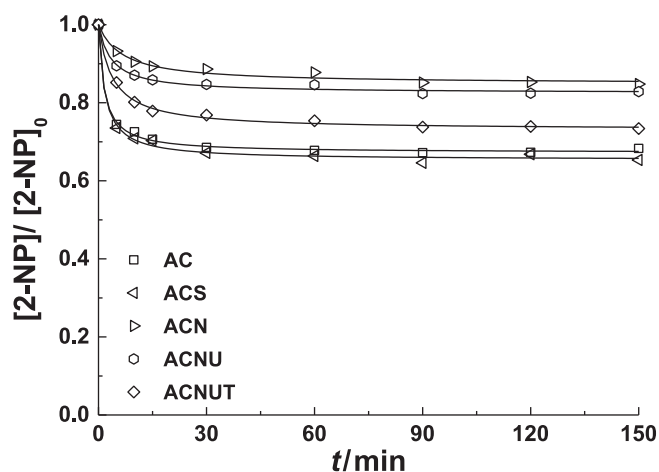
Material	<i>PZC</i>	Acidity ( $\mu\text{mol g}^{-1}$ )	Basicity ( $\mu\text{mol g}^{-1}$ )
AC	7.6	360	530
CNT	8.1	400	80
GBCM	1.3	(a)	4
CX	9.2	410	490
ACS	2.0	1000	190
ACN	1.6	2300	220
ACNU	6.1	1240	500
ACNUT	10.3	530	890
Fe <sub>473</sub> /AC	3.7	1220	420
Fe <sub>573</sub> /AC	2.2	1910	140
Fe <sub>473</sub> /ACS	3.1	1590	240
Fe <sub>573</sub> /ACS	2.0	2140	40

(a) GBCM is an unstable material under basic conditions and partially decomposes.



**Fig. 1.** Removal of 2-NP ( $100 \text{ mg L}^{-1}$ ) obtained in pure adsorption runs performed under typical conditions ( $T = 323 \text{ K}$ ,  $\text{pH } 3$  and adsorbent load  $= 0.1 \text{ g L}^{-1}$ ) with the initial four carbon materials.



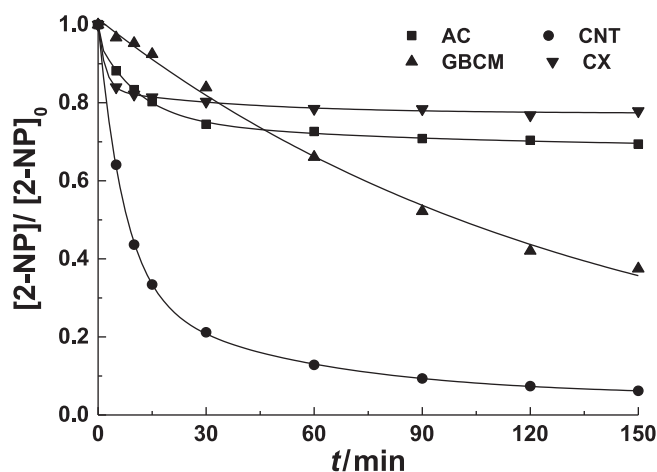


**Fig. 2.** Removal of 2-NP (100 mg L<sup>-1</sup>) obtained in pure adsorption runs performed under typical conditions ( $T=323$  K, pH 3 and adsorbent load = 0.1 g L<sup>-1</sup>) with the modified activated carbons and the original AC.

of correlations between their behaviour as adsorbents and their intrinsic characteristics becomes difficult. Nevertheless, the basic character of AC (Table 2), plus the fact that 2-NP is a weak acid [3], favours their interaction as adsorbent/adsorbate. In addition, the higher specific surface area of AC amongst the tested materials seems to contribute to the higher removal observed with this material. In fact the specific surface area seems to justify the differences observed between AC and CX. In the opposite, 2-NP adsorption on GBCM is substantially lower, which may be explained by the low specific surface area that characterizes this carbon material (Table 1). On the other hand, the importance of the surface chemistry on adsorption processes [14,15,17] is corroborated by the results obtained with the CNT, since their adsorption capacity is only slightly higher than that of GBCM, despite their much higher  $S_{\text{BET}}$ .

### 3.2.1. Modified activated carbons as adsorbents

Given that AC was found to be the best adsorbent amongst those tested (Fig. 1), and aiming to improve its intrinsic properties for the adsorption process, AC was subjected to different liquid phase, thermal and hydrothermal treatments. The removal of 2-NP in adsorption runs performed with the original AC and with the modified activated carbons (ACS, ACN, ACNU and ACNUT) is shown in Fig. 2. Although differences may fall within the associated experimental errors, it seems clear that ACS slightly improves the adsorption capacity of the original AC. All the other materials revealed lower adsorption capacity when compared to the original AC. These adsorption results confirm the interesting characteristics of activated carbons treated with sulphuric acid (ACS) reported in a previous work [15]. Taking only into consideration adsorption by electrostatic interaction forces, it would be expected that the adsorption of 2-Nitrophenol, a weak acid, would be favoured by basic materials, since 2-NP partially dissociates to the anionic form, thus favouring the interaction adsorbent/adsorbate by utilization of materials with  $PZC$  higher than the adsorption pH (3, in the present work). This mechanism explains the low adsorption performance of ACN ( $PZC = 1.6$ ) and the behaviours of AC, ACNU and ACNUT ( $PZC$  ranging from 6.1 to 10.3). In contrast to this generally accepted adsorption mechanism is the behaviour of ACS, an acidic material with a  $PZC = 2.0$ , whose performance would be initially expected to be close to that observed with ACN. Surprisingly, the adsorption performance of ACS was the best amongst the studied materials (slightly better than AC).



**Fig. 3.** Removal of 2-NP (100 mg L<sup>-1</sup>) obtained in CWPO runs performed under typical conditions ( $C_{H_2O_2} = 34.6$  mmol L<sup>-1</sup>,  $T=323$  K, pH 3 and catalyst load = 0.1 g L<sup>-1</sup>) with the initial four carbon materials.

### 3.3. CWPO experiments

The ability of the initial four carbon materials to act as catalysts in the CWPO of 2-NP was evaluated through CWPO experiments performed under the typical conditions referred in Section 2.4. The corresponding 2-NP removal curves are collected in Fig. 3. The first conclusion withdrawn from the results is that the performance of the CNT is largely superior to the performance of the other materials. A 2-NP removal higher than 90% after 150 min of reaction is observed, whilst the second best material (*i.e.*, GBCM) is able to remove only about 60% during the same time interval. Furthermore, a 2-NP removal of about 80% is reached in only 30 min of reaction with the CNT. As a first tentative explanation, the astonishing results obtained with CNT were attributed to the presence of iron oxides resulting from their synthesis procedure. In order to better understand the mechanisms involved, CNT were selected for further studies in this work (Section 3.3.1). Regarding GBCM, the high density of sulphonic acid groups on their surface [22] is apparently responsible for the high activity revealed by this catalyst, since sulphonic acid groups are known to increase the efficiency of CWPO processes [14]. Unlike GBCM and CNT, the performance evidenced by AC and CX is relatively poor. The shape of the corresponding removal curves (reaching a plateau) and the comparison with the adsorption removals presented in section 3.2 lead to the conclusion that these materials are not active for CWPO of 2-NP and that the removal of the pollutant is mainly due to pure adsorption.

For better comparison, the pure adsorption and CWPO removals of 2-NP after 150 min with the initial four carbon materials are compiled in Table 3. Considering the pure adsorption process, it is observed that AC and CX allow superior 2-NP removals. Analysis of these results in conjunction with those from CWPO experiments allows to confirm that AC and CX are not active for the CWPO of

**Table 3**  
Removal of 2-NP ( $\pm 2\%$ ) obtained by pure adsorption and CWPO with the initial four carbon materials after 150 min under typical conditions ( $T=323$  K, pH 3, adsorbent/catalyst load = 0.1 g L<sup>-1</sup> and, in CWPO runs,  $C_{H_2O_2} = 34.6$  mmol L<sup>-1</sup>).

Material	2-NP removal			
	%		mg g <sup>-1</sup>	
	Adsorption	CWPO	Adsorption	CWPO
AC	32	31	316	304
CNT	11	94	108	929
GBCM	7	63	74	612
CX	27	22	271	221

**Table 4**

2-NP removals ( $\pm 2\%$ , after 30 min and 150 min of CWPO) and Fe concentration in the treated solutions ( $\pm 1\%$ ) at the end of CWPO runs performed with CNT and with activated carbon supported iron catalysts.

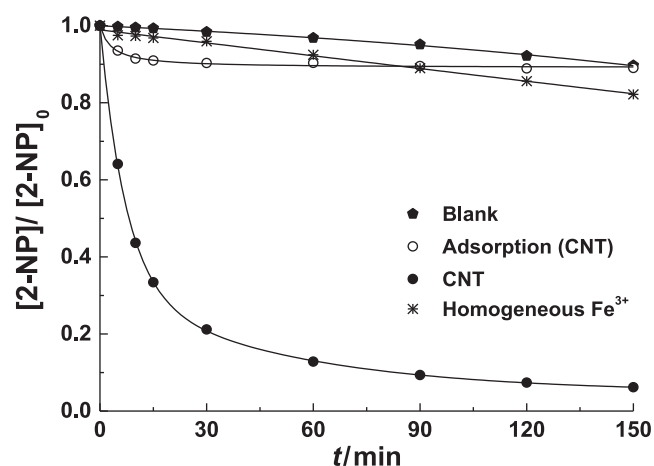
Material	2-NP removal (%)		Fe leached ( $\text{mg L}^{-1}$ )
	30 min	150 min	
CNT	79	94	0.02
Fe <sub>473</sub> /AC	41	98	0.75
Fe <sub>473</sub> /ACS	79	99	1.85
Fe <sub>573</sub> /AC	94	100	2.97
Fe <sub>573</sub> /ACS	96	100	2.65

2-NP. In fact, the removals observed by CWPO with these materials are even lower than those observed by pure adsorption, which is explained by reduced adsorption caused by competition between 2-NP and  $\text{H}_2\text{O}_2$  for the available adsorption sites. On the contrary, CNT and GBCM are very active for CWPO of 2-nitrophenol, the removals of 2-NP being widely enhanced in CWPO experiments, compared to the removals observed by pure adsorption. More precisely, when using CNT and GBCM, the 2-NP removals observed by CWPO after 150 min increase 83% and 56%, respectively, compared with the removals observed in the pure adsorption experiments performed under the same conditions. When using CNT as catalyst, a 2-NP removal up to  $929 \text{ mg g}^{-1}$  is achieved by CWPO. Blank experiments performed under the same operating conditions reveal that the non-catalytic oxidation of 2-NP promoted by  $\text{H}_2\text{O}_2$  ( $34.6 \text{ mmol L}^{-1}$ ) is only about 10% after 150 min.

### 3.3.1. CNT vs. supported iron catalysts

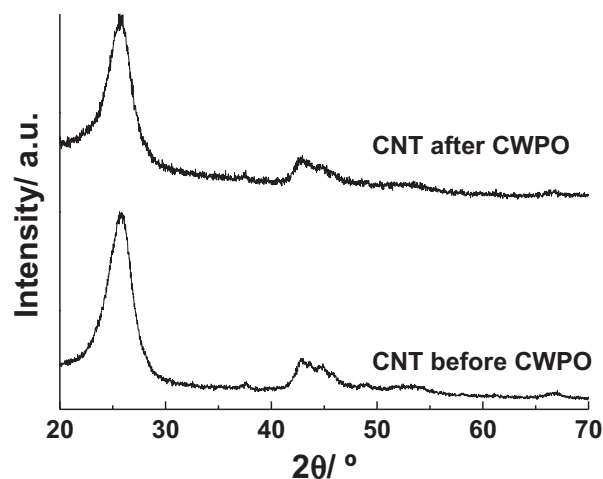
Amongst the tested carbon materials, CNT revealed the highest catalytic activity for the CWPO of 2-NP (Table 3). However, as mentioned in Section 2.2, CNT contain alumina and iron oxides in their composition as impurities resulting from their synthesis procedure. Thus, after the CWPO run, the carbon content of the CNT was quantified by thermogravimetric analysis (TGA), a value of 91.7 wt.% being obtained, suggesting that some of the impurities resulting from the CNT production may be leached to solution during the CWPO run. Bearing these results in mind, it would be reasonable to argue that the observed activity is due to leaching of iron species into solution, since it is well known that iron ions are very active catalysts in CWPO (Fenton process) [10]. In order to evaluate this possibility, the Fe content in the treated solution at the end of the CWPO experiment with CNT was determined. The result obtained is given in Table 4 ( $0.02 \text{ mg L}^{-1}$ ), being concluded that lixiviated Fe is very low, and far below the European Economic Community standards for discharge of treated waters –  $2 \text{ mg L}^{-1}$ . Even though, the possible effect of homogeneous catalysis promoted by the amount of Fe leached during CWPO was simulated by using a  $\text{Fe}^{3+}$  solution as catalyst with the same concentration as the leached Fe. This effect, together with those previously determined (*i.e.*, pure adsorption and non-catalytic removals), is quantified in Fig. 4. It is clearly concluded that the contributions of pure adsorption, non-catalytic and homogeneous catalytic removals are negligible, suggesting that CNT are effectively active catalysts for CWPO. Furthermore, XRD analysis of CNT (before and after CWPO) was performed, the resulting diffractograms being shown in Fig. 5. It can be observed that the two CNT samples show similar XRD profiles, suggesting that no significant distortion of CNT structure results from their use in the CWPO process.

As the results and conclusions gathered from Figs. 4 and 5 are quite thrilling, the catalytic activity of CNT and Fe leached during CWPO were further compared with classical activated carbon supported iron catalysts, which are known to be very efficient in CWPO processes [10]. For that purpose, the iron catalysts supported on activated carbons produced as described in Section 2.2.2 were



**Fig. 4.** Removal of 2-NP ( $100 \text{ mg L}^{-1}$ ) obtained in the study performed with the CNT ( $0.1 \text{ g L}^{-1}$ ) and  $\text{Fe}^{3+}$  ( $0.02 \text{ mg L}^{-1}$ ) under typical conditions ( $T=323 \text{ K}$ ,  $\text{pH } 3$  and, in CWPO runs,  $\text{C}_{\text{H}_2\text{O}_2} = 34.6 \text{ mmol L}^{-1}$ ). Non-catalytic removal (blank) is also given.

tested in the CWPO of 2-NP at the typical operating conditions; then, at the end of each run, the Fe content of the treated solutions was determined. The corresponding results are given in Table 4. As observed, 2-NP removals by CWPO are higher when using any of the activated carbon supported iron catalysts. However, Fe leaching is also much higher. In order to understand if the leached Fe could be responsible for the removals observed, the effect of homogeneous catalysis promoted by the amount of Fe leached during CWPO was simulated using an  $\text{Fe}^{3+}$  solution as catalyst with the same concentration of Fe as the Fe lixiviated in the CWPO experiment with Fe<sub>473</sub>/AC (*i.e.*,  $0.75 \text{ mg L}^{-1}$ , the experiment where the concentration of leached Fe was lowest amongst the experiments performed with activated carbon supported iron catalysts). The result shows that 2-NP removal by CWPO after 150 min at these conditions reaches 99.5%, suggesting that the contribution of homogeneous catalysis promoted by leached Fe is, in this case, the major mechanism of 2-NP removal when the supported iron catalysts studied in this work are considered for CWPO. This is the opposite of the results observed with CNT, which emphasizes the importance of the previous findings, and thus we may conclude that the combined catalytic activity of the CNT and the low Fe leaching observed in CWPO make this material more effective for CWPO than classical activated carbon supported iron catalysts. In addition, the activity of CNT is comparable to that of carbon nanotubes supported iron catalysts



**Fig. 5.** XRD spectra of CNT (before and after the CWPO process).

reported in the literature for the removal of phenol under similar conditions [44], with the substantial advantage that CNT can be used directly as produced and without any added metal phase.

In order to better assess the global catalytic performance of CNT, complementary experiments were performed to quantify TOC removal and to identify and quantify intermediate low molecular weight carboxylic acids in the degradation of 2-NP. The TOC removal obtained was modest, since it reaches only 13% of its initial content, and maleic acid was the only identified carboxylic acid, its concentration increasing continuously until  $4.8 \text{ mg L}^{-1}$  after 150 min of reaction. Oxalic acid, considered as the main responsible for iron leaching in supported iron catalysts [12,45], was not detected, which may explain the low level of Fe leached during the CWPO run performed with CNT. Nevertheless, CNT stability in the presence of oxalic acid was assessed through an experiment performed considering  $[\text{oxalic acid}] = 100 \text{ mg L}^{-1}$ , CNT load =  $0.1 \text{ g L}^{-1}$ ,  $T = 323 \text{ K}$  and pH 3. Results show that Fe leached after 150 min under these extreme conditions amounts to only  $0.09 \text{ mg L}^{-1}$ , which is comparable with the results obtained with a stable activated carbon catalyst prepared by chemical activation of lignin from black liquors [46].

Summarizing, with the set of results obtained in the CWPO experiments carried out with CNT, we may conclude that this catalyst shows high catalytic activity for 2-NP removal and low Fe leaching, but with a rather low mineralization. Further studies are now needed in order to improve the level of mineralization achieved.

#### 4. Conclusions

Amongst the tested carbon materials, with distinct morphological and chemical properties, the classical activated carbons are the best solution for the removal of 2-NP by pure adsorption, exhibiting removals up to  $316 \text{ mg g}^{-1}$ . The carbon samples produced by modification of the original AC have increased porosity but, except for the sample treated with sulphuric acid, the intrinsic ability to adsorb 2-NP was not improved because of the acidity of the surface.

CNT and GBCM were found as very effective materials for 2-NP CWPO, since the removal is greatly enhanced compared to pure adsorption. Amongst all tested materials, CNT was the catalyst with higher catalytic activity in the CWPO of 2-NP. Due to the existence of iron oxides in the composition of CNT, the lixiviation of Fe during CWPO was quantified and considered negligible. The high catalytic activity of CNT and the low Fe leaching observed in CWPO make this catalyst a promising system for CWPO, with superior performances to that of classical activated carbon supported iron catalysts.

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#### References

- [1] K.W. Brown, K.C. Donnelly, *Hazardous Waste and Hazardous Materials* 5 (1988) 1–30.
- [2] S. Sporstøl, K. Urdal, H. Drangsholt, N. Gjø, *International Journal of Environment Analytical Chemistry* 21 (1985) 129–138.
- [3] USATSDR, Toxicological profile for nitrophenols, Agency for Toxic Substances and Disease Registry, Atlanta, U.S., 1992.
- [4] USEPA, Treatability manual volume I, Office of Research and Development, Environmental Protection Agency, Washington D.C., U.S., 1980.
- [5] USEPA, Health effects assessment for nitrophenols, Office of Research and Development, Environmental Protection Agency, Cincinnati, U.S., 1987.
- [6] P.R. Gogate, A.B. Pandit, *Advances in Environmental Research* 8 (2004) 501–551.
- [7] S. Navalón, M. Alvaro, H. García, *Applied Catalysis B* 99 (2010) 1–26.
- [8] C.W. Jones, *Applications of Hydrogen Peroxide and Derivatives*, The Royal Society of Chemistry, Cambridge, UK, 1999.
- [9] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, *Applied Catalysis B* 47 (2004) 219–256.
- [10] J.J. Pignatello, E. Oliveros, A. MacKay, *Critical Reviews in Environment Science and Technology* 36 (2006) 1–84.
- [11] J.H. Ramirez, F.J. Maldonado-Hódar, A.F. Pérez-Cadenas, C. Moreno-Castilla, C.A. Costa, L.M. Madeira, *Applied Catalysis B* 75 (2007) 312–323.
- [12] J.A. Zazo, J.A. Casas, A.F. Mohedano, J.J. Rodríguez, *Applied Catalysis B* 65 (2006) 261–268.
- [13] A. Dhauouadi, N. Adhoum, *Applied Catalysis B* 97 (2010) 227–235.
- [14] H.T. Gomes, S.M. Miranda, M.J. Sampaio, J.L. Figueiredo, A.M.T. Silva, J.L. Faria, *Applied Catalysis B* 106 (2011) 390–397.
- [15] H.T. Gomes, S.M. Miranda, M.J. Sampaio, A.M.T. Silva, J.L. Faria, *Catalysis Today* 151 (2010) 153–158.
- [16] F. Lücking, H. Köser, M. Jank, A. Ritter, *Water Research* 32 (1998) 2607–2614.
- [17] R.S. Ribeiro, N.A. Fathy, A.A. Attia, A.M.T. Silva, J.L. Faria, H.T. Gomes, *Chemical Engineering Journal* 195–196 (2012) 112–121.
- [18] S. Navalón, A. Dhakshinamoorthy, M. Alvaro, H. García, *ChemSusChem* 4 (2011) 1712–1730.
- [19] P. Serp, J.L. Figueiredo, *Carbon Materials for Catalysis*, John Wiley & Sons, Inc., Hoboken, NJ, 2009.
- [20] P. Serp, M. Corrias, P. Kalck, *Applied Catalysis A* 253 (2003) 337–358.
- [21] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, M. Mahdavi, *Monatshefte für Chemie* 140 (2009) 1489–1494.
- [22] B.L.A. Prabhavathi Devi, K.N. Gangadhar, P.S. Sai Prasad, B. Jagannadh, R.B.N. Prasad, *ChemSusChem* 2 (2009) 617–620.
- [23] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, *Solid State Sciences* 12 (2010) 1029–1034.
- [24] O. Abdelwahab, N.K. Amin, E.S.Z. El-Ashtoukhy, *Journal of Hazardous Materials* 163 (2009) 711–716.
- [25] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, *Desalination* 261 (2010) 3–18.
- [26] M. Diao, N. Ouédraogo, L. Baba-Moussa, P. Savadogo, A. N'Guessan, I.N. Bassolé, M. Dicko, *Biodegradation* 22 (2011) 389–396.
- [27] E.-S.Z. El-Ashtoukhy, Y.A. El-Taweel, O. Abdelwahab, E.M. Nassef, *International Journal of Electrochemical Science* 8 (2013) 1534–1550.
- [28] Y. Kurata, Y. Ono, Y. Ono, *Journal of Material Cycles and Waste Management* 10 (2008) 144–152.
- [29] X. Peng, Y. Yu, C. Tang, J. Tan, Q. Huang, Z. Wang, *Science of the Total Environment* 397 (2008) 158–166.
- [30] Arkema, Graphistrength® C100 data sheet for product development, France, 2006.
- [31] L.W. Huang, O. Elkedim, M. Nowak, M. Jurczyk, R. Chassagnon, D.W. Meng, *International Journal of Hydrogen Energy* 37 (2012) 1538–1545.
- [32] Sigma-Aldrich, Multi-walled carbon nanotubes (ref. 677248) material safety data sheet, Version 5.0, St. Louis M.O., U.S., 2013.
- [33] B. Krause, M. Mende, P. Pötschke, G. Petzold, *Carbon* 48 (2010) 2746–2754.
- [34] X. Wang, S.C. Jana, *Polymer* 54 (2013) 750–759.
- [35] H.T. Gomes, B.F. Machado, A. Ribeiro, I. Moreira, M. Rosário, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, *Journal of Hazardous Materials* 159 (2008) 420–426.
- [36] R.P. Rocha, J.P.S. Sousa, A.M.T. Silva, M.F.R. Pereira, J.L. Figueiredo, *Applied Catalysis B* 104 (2011) 330–336.
- [37] G. Newcombe, R. Hayes, M. Drikas, *Colloids and Surfaces A* 78 (1993) 65–71.
- [38] M.A. Ferro-García, J. Rivera-Utrilla, I. Bautista-Toledo, C. Moreno-Castilla, *Langmuir* 14 (1998) 1880–1886.
- [39] J. Rivera-Utrilla, I. Bautista-Toledo, M.A. Ferro-García, C. Moreno-Castilla, *Journal of Chemical Technology and Biotechnology* 76 (2001) 1209–1215.
- [40] Á.C. Apolinário, A.M.T. Silva, B.F. Machado, H.T. Gomes, P.P. Araújo, J.L. Figueiredo, J.L. Faria, *Applied Catalysis B* 84 (2008) 75–86.
- [41] F. Duarte, F.J. Maldonado-Hódar, L.M. Madeira, *Applied Catalysis B* 103 (2011) 109–115.
- [42] J.H. Ramirez, C.A. Costa, L.M. Madeira, G. Mata, M.A. Vicente, M.L. Rojas-Cervantes, A.J. López-Peinado, R.M. Martín-Aranda, *Applied Catalysis B* 71 (2007) 44–56.
- [43] R. Giordano, P. Serp, P. Kalck, Y. Kihn, J. Schreiber, C. Marhic, J.-L. Duvail, *European Journal of Inorganic Chemistry* 2003 (2003) 610–617.
- [44] Q. Liao, J. Sun, L. Gao, *Colloids and Surfaces A* 345 (2009) 95–100.
- [45] A. Rey, M. Faraldos, J.A. Casas, J.A. Zazo, A. Bahamonde, J.J. Rodríguez, *Applied Catalysis B* 86 (2009) 69–77.
- [46] J.A. Zazo, J. Bedia, C.M. Fierro, G. Pliego, J.A. Casas, J.J. Rodríguez, *Catalysis Today* 187 (2012) 115–121.